



# Cluster Modeling of Network-Forming Amorphization Pathways in $\text{As}_x\text{S}_{100-x}$ Arsenicals ( $50 \leq x \leq 57$ ) Diven by Nanomilling

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## Abstract

Complete hierarchy of network amorphization scenarios initiated in  $\text{As}_x\text{S}_{100-x}$  nanoarsenicals within  $\text{As}_4\text{S}_4$ - $\text{As}_4\text{S}_3$  cut-Sect. ( $50 \leq x \leq 57$ ) is reconstructed employing materials-computational approach based on ab-initio quantum-chemical modeling code (CINCA). Under nanostructurization due to high-energy mechanical milling, the inter-crystalline transformations to nanoscopic  $\beta$ - $\text{As}_4\text{S}_4$  phase accompanied by appearance of covalent-network amorphous matrix are activated. General amorphization trend under nanomilling obeys tending from molecular cage-like structures to optimally-constrained covalent-bonded networks compositionally invariant with parent arsenical. The contribution of amorphization paths in nanoarsenicals is defined by their chemistry with higher molecular-to-network barriers proper to  $\text{As}_4\text{S}_3$ -rich alloys. The generated amorphous phase is intrinsically decomposed, possessing double- $T_g$  relaxation due to stoichiometric ( $x = 40$ ) and non-stoichiometric ( $x > 40$ ) sub-networks, which are built of  $\text{AsS}_{3/2}$  pyramids and As-rich arrangement keeping (i) two separated As-As bonds derived from realgar-type molecules, (ii) two neighboring As-As bonds derived from pararealgar-type molecules or (iii) three neighboring As-As bonds in triangle-like geometry derived from dimorphite-type molecules. Compositional invariance of nanoamorphous phase is ensured by growing sequence of network-forming clusters with average coordination numbers  $Z$  in the row ( $\text{As}_2\text{S}_{4/2}$ ,  $Z = 2.50$ ) – ( $\text{As}_3\text{S}_{5/2}$ ,  $Z = 2.55$ ) – ( $\text{As}_3\text{S}_{3/2}$ ,  $Z = 2.67$ ). Diversity of main molecular-to-network amorphizing pathways in nanoarsenicals is reflected on the unified potential energy landscape specified for boundary  $\text{As}_4\text{S}_4$  and  $\text{As}_4\text{S}_3$  components.

**Keywords** Arsenicals · Amorphization · *Ab-initio* quantum-chemical modeling · Molecular cluster · Nanomilling

## Introduction

The family of binary *arsenic sulphides*  $\text{As}_x\text{S}_{100-x}$  [1–6], often referred to as *arsenicals* due to their anticancer therapeutic functionality [7], are accepted as representatives of canonical substances, where diverse structure-conformation tendencies can be revealed in dependence on their chemistry. Thus, at the moderated As content in these *thioarsenide* alloys close to stoichiometry  $\text{As}_2\text{S}_3$  (viz.  $\text{As}_{40}\text{S}_{60}$ ), competitive matrix *amorphization* (*vitrification*) and layer-type conformation (*crystallization*) processes occur, while in As-rich  $\text{As}_x\text{S}_{100-x}$  compounds (where  $x$  exceeds 40) the latter are replaced by molecular-crystallization tendencies accompanied by stabilization of  $\text{As}_4\text{S}_n$  cage-like molecules ( $n = 5, 4, 3$ ) [8–10].

Under full saturation of covalent chemical bonding in respect to the Mott's  $8-N$  rule [3], which is characteristic feature of many chalcogenide compounds allowing their consideration in terms of the average coordination number  $Z$  (the number of covalent bonds per atom) [5], this As-S system reveals unprecedented glass-forming ability in a vicinity of arsenic trisulphide  $\text{As}_2\text{S}_3$  [4]. That is why the glassy  $g$ - $\text{As}_2\text{S}_3$  prepared by melt-quenching cannot be crystallized during prolonged thermal treatment even above glass-transition temperature  $T_g$  [2, 3], despite the known fact on existing of isocompositional mineral with layered crystalline structure (the orthorhombic orpiment possessing space group  $P2_1/n$ ) [8]. Trigonal  $\text{AsS}_{3/2}$  pyramids (as main structural motives of this glass-former) interconnected by S atoms in so-called corner- or atom-shared links form basis for under-stoichiometric covalent networks of S-rich  $\text{As}_x\text{S}_{100-x}$  arsenicals ( $x < 40$ ), realized

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due to polymerization (bridging) properties of  $-S_n-$  chains. Therefore, the compositional domain of stable glass-formers extends in binary As-S system to  $Z \sim 2.16$  dependently on melt-quenching route (it means that  $g\text{-As}_{16}\text{S}_{84}$  possesses competitive S separation-agglomeration properties) [2–4]. Within this range of S-rich  $\text{As}_x\text{S}_{100-x}$  arsenicals up to stoichiometric  $\text{As}_2\text{S}_3$  ( $2.16 < Z \leq 2.40$ ), this system demonstrates few anomalies like *instability onsets* in cluster-forming energies [6], which were mistakenly accepted as “signatures” of intermediate optimally-constrained (rigid and stress-free) phases in covalent-bonded network substances [11].

Controversially, under enlarged As content in this  $\text{As}_x\text{S}_{100-x}$  system over  $\text{As}_2\text{S}_3$  stoichiometry, the network-forming tendency rapidly disappears at  $Z \sim 2.44\text{--}2.46$  on a cost of partially crystallized arrangement of *thioarsenide*  $\text{As}_4\text{S}_n$  molecules ( $n = 5, 4, 3$ ) [1–4]. These cage-like entities (having no dangling bonds or terminated inter-cluster links) serve as main blocks for molecular crystals of some minerals, such as uzonite  $\text{As}_4\text{S}_5$  ( $Z = 2.44$ ), realgar  $\alpha\text{-As}_4\text{S}_4$  ( $Z = 2.50$ ), bonazitte or  $\beta\text{-As}_4\text{S}_4$  ( $Z = 2.50$ ), pararealgar  $\text{As}_4\text{S}_4$  ( $Z = 2.50$ ), as well as  $\alpha/\beta$ -dimorphite  $\text{As}_4\text{S}_3$  ( $Z = 2.57$ ) [4, 8]. The former (the uzonite  $\text{As}_4\text{S}_5$ ) along with *tetra-arsenic tetrasulphide*  $\text{As}_4\text{S}_4$  possessing four different crystallographic polymorphs seem to be most plausible candidates for devitrification in the group of melt-quenched  $\text{As}_x\text{S}_{100-x}$  alloys at  $x > 44$ .

Notwithstanding, phase equilibria become more complicated with progressive increase in As content in  $\text{As}_x\text{S}_{100-x}$  arsenicals, resulting in the second glass-forming region at  $51 \leq x \leq 66$ . Hruby [1] was the first who considered these glasses as metastable plastic phases with  $T_g$  below room temperature. In his opinion, thermodynamically stable glasses of these compositions (with  $Z = 2.51\text{--}2.66$ ) do not exist. The second glass-forming region in these thioarsenide alloys was shown to be superimposed with stabilization domain of *tetra-arsenic trisulphide* polymorphs  $\text{As}_4\text{S}_3$  ( $Z = 2.57$ ) [12, 13], meaning the crucial role of spherically-symmetric  $\text{As}_4\text{S}_3$  cage-like molecules [14]. The plastic-crystalline rhombohedral modification of this dimorphite-type  $\text{As}_4\text{S}_3$  phase as found by Chattopadhyay et al. [15] and further generalized by Blachnik and Wickel [16] was accepted as responsible for additional rotational disorder in these glass-formers.

This finding was further proved by Aitken for ternary  $\text{Ge}_x\text{As}_y\text{S}_{100-x-y}$  glasses with As:Ge ratio approaching  $\sim 17:1$  [17, 18]. It was also shown [19–21] that under nanostructurization caused by external influence such as high-energy mechanical milling (nanomilling), the complicated inter-crystalline phase transformations towards nanocrystalline  $\beta\text{-As}_4\text{S}_4$  polymorph (nc- $\beta\text{-As}_4\text{S}_4$ ) accompanied by appearance of isocompositional amorphous phase having covalent network were activated in these

arsenicals along realgar-dimorphite  $\text{As}_4\text{S}_4\text{--As}_4\text{S}_3$  cut-Sect. ( $2.50 \leq Z \leq 2.57$ ).

In this work, the amorphization scenarios in  $\text{As}_x\text{S}_{100-x}$  arsenicals along  $\text{As}_4\text{S}_4\text{--As}_4\text{S}_3$  line ( $50 \leq x \leq 57$ ) will be recognized employing the advanced materials-computational approach [12, 22] developed at the basis of the authorized *ab-initio* quantum-chemical modeling code (CINCA) [6, 23, 24].

## Method: the CINCA Modeling of Molecular-Network Conformations in Covalent Substances

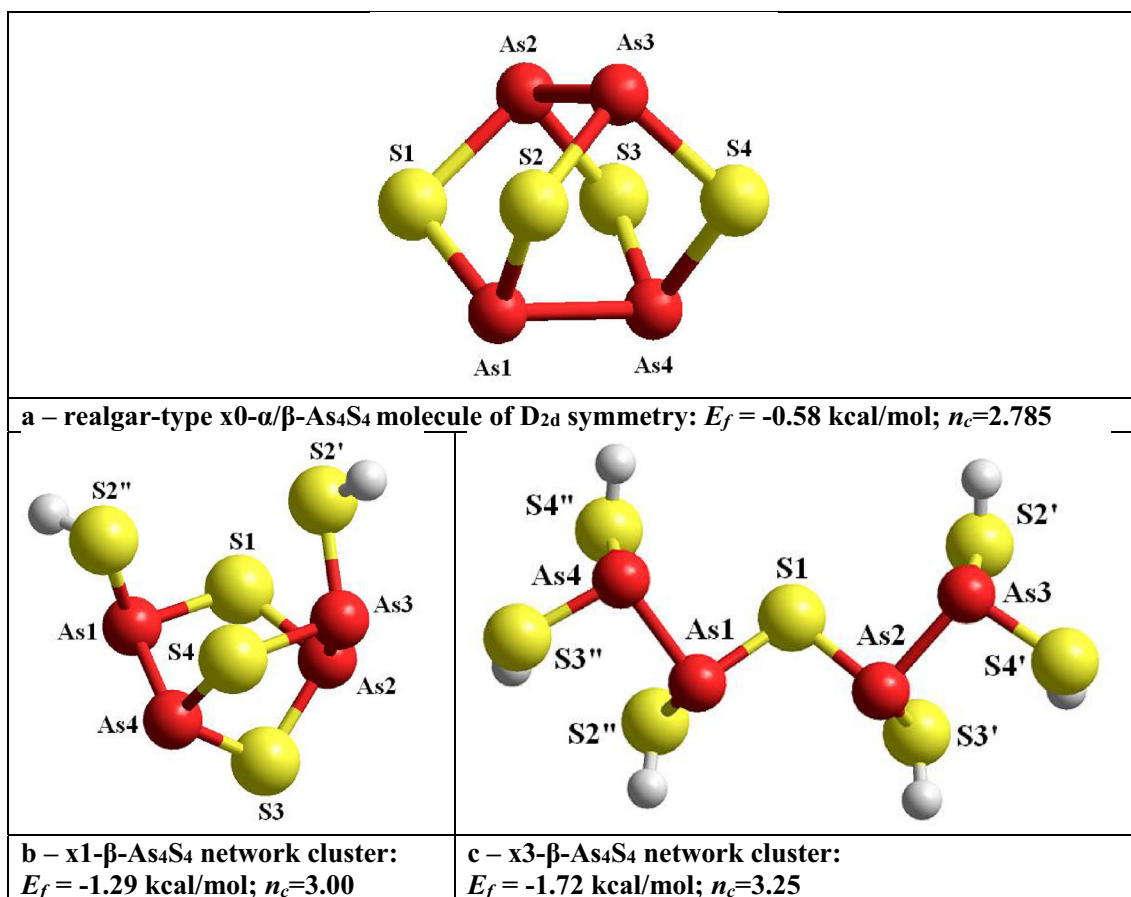
The geometrically-optimized configurations of  $\text{As}_4\text{S}_n$  cage-like molecules ( $n = 4, 3$ ) and their network-forming derivatives responsible for amorphization in  $\text{As}_x\text{S}_{100-x}$  arsenicals along  $\text{As}_4\text{S}_4\text{--As}_4\text{S}_3$  cut-line were simulated with *ab-initio* quantum-chemical cluster-modeling algorithm CINCA (cation-interlinked network cluster approach) [6, 23, 24]. Network-forming clusters were reconstructed by breaking respective  $\text{As}_4\text{S}_4$  or  $\text{As}_4\text{S}_3$  molecules on distinct fragments linking them with surrounding matrix by  $S_{1/2}\dots S_{1/2}$  bridging chains. The HyperChem Release 7.5 program package based on restricted Hartree–Fock self-consistent field method with split-valence double-zeta basis set and single polarization function 6-311G\* [25–27] was employed for cluster energy calculations. Final geometrical optimization and single-point energy calculations for selected clusters were performed employing the Fletcher-Reeves conjugate gradient method until the root-mean-square gradient of  $0.1 \text{ kcal}/(\text{\AA}\cdot\text{mol})$  was reached. The calculated cluster-forming energies  $E_f$  were corrected on the energy of terminated H atoms used to transform the network-forming clusters into molecular self-consistent precursors according to the procedure developed elsewhere [27, 28], and finally determined in respect to the energy of single trigonal  $\text{AsS}_{3/2}$  pyramid ( $E_f = -79.404 \text{ kcal/mol}$ ) [6, 23].

Thus, the developed cluster-modeling code CINCA allows quantitative comparison between molecular- and network-forming tendencies in covalent substances, parameterizing adequately competitive crystallization-amorphization scenarios.

## Results and Discussion

### Cluster Modeling of Amorphization Paths Derived from Realgar-Type $\alpha/\beta\text{-As}_4\text{S}_4$ Polymorphs

The quantum-chemical model of realgar-type  $\text{As}_4\text{S}_4$  molecule (see Fig. 1a) was developed in our preliminary



**Fig. 1** Geometrically-optimized configurations of realgar-type  $\alpha/\beta$ -As<sub>4</sub>S<sub>4</sub> cage-like molecule (**a**) and its energetically favorable network derivatives formed from As<sub>4</sub>S<sub>5</sub>H<sub>2</sub> molecule by single  $\times 1$ -break in S1 position (**b**), and from As<sub>4</sub>S<sub>7</sub>H<sub>6</sub> molecule by triple  $\times 3$ -break in S1-

S2-S3 positions (**c**). The terminated H atoms are grey-colored, S and As atoms are yellow- and red-depicted, and covalent bonds between atoms are denoted by respectively colored sticks [19, 22]

research [29]. This cage-like molecule of  $D_{2d}$  symmetry built of 8 heteronuclear As-S bonds and 2 homonuclear As-As bonds in separated mutually orthogonal configuration evolves 8 small rings (4 pentagons and 4 hexagons), thus resulting in under-constrained structural motive possessing average number of topological constraints per atom  $n_c = 2.875$  (in respect to the Phillips-Thorpe constraint-counting algorithm [30–32] applied to stretching and bending forces ascribed to bonds in this molecule). The same symmetric As<sub>4</sub>S<sub>4</sub> molecule (with intramolecular bond lengths and angles close to those refined from realistic crystalline structures) is character for mineral realgar  $\alpha$ -As<sub>4</sub>S<sub>4</sub> [33, 34], synthetic  $\beta$ -As<sub>4</sub>S<sub>4</sub> [35] and its natural analogue (mineral bonazziite As<sub>4</sub>S<sub>4</sub> [36]). The calculated cluster-forming energy  $E_f$  for this molecule (in respect to the energy of AsS<sub>3/2</sub> pyramid) equals  $-0.58$  kcal/mol (Table 1) [19, 22], the value dominated over all molecular and network-forming arsenical clusters within compositional range of interest ( $2.50 \leq Z \leq 2.57$ ).

The most plausible amorphization scenarios in arsenic monosulphide AsS (viz. As<sub>4</sub>S<sub>4</sub>) are related to high-

temperature *tetra-arsenic tetrasulphide*  $\beta$ -As<sub>4</sub>S<sub>4</sub> polymorph [10, 19, 20]. This specificity is revealed due to lower barrier of  $\alpha$ -As<sub>4</sub>S<sub>4</sub>-to- $\beta$ -As<sub>4</sub>S<sub>4</sub> transition [37] as compared with nanostructurization-driven amorphization from each of these phases (low-temperature  $\alpha$ -As<sub>4</sub>S<sub>4</sub> or high-temperature  $\beta$ -As<sub>4</sub>S<sub>4</sub>), provided direct low-to-high-temperature phase transformation was not inhibited.

Among a group of network-forming derivatives from this realgar-type cage-like molecule ( $\beta$ -As<sub>4</sub>S<sub>4</sub>), the smallest cluster-forming energy  $E_f = -1.29$  kcal/mol is achieved for single-broken  $\times 1$ - $\beta$ -As<sub>4</sub>S<sub>4</sub> cluster (see Table 1) derived from As<sub>4</sub>S<sub>5</sub>H<sub>2</sub> molecular precursor as shown on Fig. 1b [19, 22]. This cluster having one hexagon and two pentagons in atomic arrangement is optimally-constrained since  $n_c = 3.00$ , which is in strict respect to space dimensionality ( $D = 3$ ). Therefore, covalent-bonded structures built of such clusters are most favorable for amorphization. Because of low barrier with ground state of As<sub>4</sub>S<sub>4</sub> molecule due to  $\Delta E_f = (1.29 - 0.58)$  kcal/mol = 0.71 kcal/mol, the expected molecular-to-network transformation occurs even in directly synthesized arsenic monosulphide, being a

**Table 1** Cluster-forming energies  $E_f$  (in respect to the energy of  $\text{AsS}_{3/2}$  pyramid) for network-forming derivatives from realgar-type  $\beta\text{-As}_4\text{S}_4$  molecule (atomic labels refer to Fig. 1a) [19, 22]

Molecular prototype	Network/molecular cluster, and respective cluster-forming scenario	Number of rings: hexagons/pentagons	$n_c$	$E_f$ (kcal/mol)
$\beta\text{-As}_4\text{S}_4$	no break ( $\times$ 0-break)	4/4	2.875	- 0.58
$\text{As}_4\text{S}_5\text{H}_2$	$\times$ 1- $\beta\text{-As}_4\text{S}_4$ , $\times$ 1-break in S1	1/2	3.00	- 1.29
$\text{As}_4\text{S}_6\text{H}_4$	$\times$ 2-1- $\beta\text{-As}_4\text{S}_4$ , $\times$ 2-break in S1-S3	0/1	3.125	- 3.47
$\text{As}_4\text{S}_6\text{H}_4$	$\times$ 2-2- $\beta\text{-As}_4\text{S}_4$ , $\times$ 2-break in S1-S4	1/0	3.25	- 12.59
$\text{As}_4\text{S}_7\text{H}_6$	$\times$ 3- $\beta\text{-As}_4\text{S}_4$ , $\times$ 3-break in S1-S2-S3	0/0	3.25	- 1.72
$\text{As}_4\text{S}_8\text{H}_8$	$\times$ 4- $\beta\text{-As}_4\text{S}_4$ , $\times$ 4-break in S1-S2-S3-S4	0/0	3.25	- 1.72

source of uncontrolled spontaneous amorphization [10, 19, 38–40].

An alternative path of induced amorphization in  $\beta\text{-As}_4\text{S}_4$  is related to  $\times$  3- $\beta\text{-As}_4\text{S}_4$  network-forming cluster prototyped by  $\text{As}_4\text{S}_7\text{H}_6$  molecule which appears as triple-broken derivative from realgar-type  $\text{As}_4\text{S}_4$  molecule possessing chain structure without small rings (see Fig. 1c) [19, 22]. Despite evidently over-constrained constitution (in view of  $n_c = 3.25$ ), the small  $E_f$  value approaching - 1.72 kcal/mol is character for this cluster (see Table 1), resulting in low molecular-to-network barrier  $\Delta E_f = 1.14$  kcal/mol [19]. This cluster is commensurable (within  $\pm 0.03$  kcal/mol error-bar proper to CINCA calculations [23]) with other one, the quadruple-broken  $\times$  4- $\beta\text{-As}_4\text{S}_4$  (or, alternatively,  $\text{As}_2\text{S}_{4/2}$  cluster) obtained by breaking in all S atom positions, thus keeping separated As-As bond in network. These  $\times$  3- $\beta\text{-As}_4\text{S}_4$  clusters surely dominate in nanostructured arsenicals (nanoarsenicals) in view of lower number of covalent bonds destructed in  $\times$  0- $\beta\text{-As}_4\text{S}_4$  molecule.

Thus, full variety of amorphization scenarios derived from  $\beta\text{-As}_4\text{S}_4$  phase can be depicted on potential energy landscape as shown on Fig. 2. The above network-forming derivatives ( $\times$  1- $\beta\text{-As}_4\text{S}_4$  and  $\times$  3- $\beta\text{-As}_4\text{S}_4$ ) evidently prefer over other variants of network clustering originated in part due to double-breaking of covalent bonds in realgar-type  $\text{As}_4\text{S}_4$  molecule ( $\times$  2-1- $\beta\text{-As}_4\text{S}_4$  and  $\times$  2-2- $\beta\text{-As}_4\text{S}_4$ ) [19].

### Cluster Modeling of Amorphization Scenarios Activated from Pararealgar $\text{As}_4\text{S}_4$ Phase

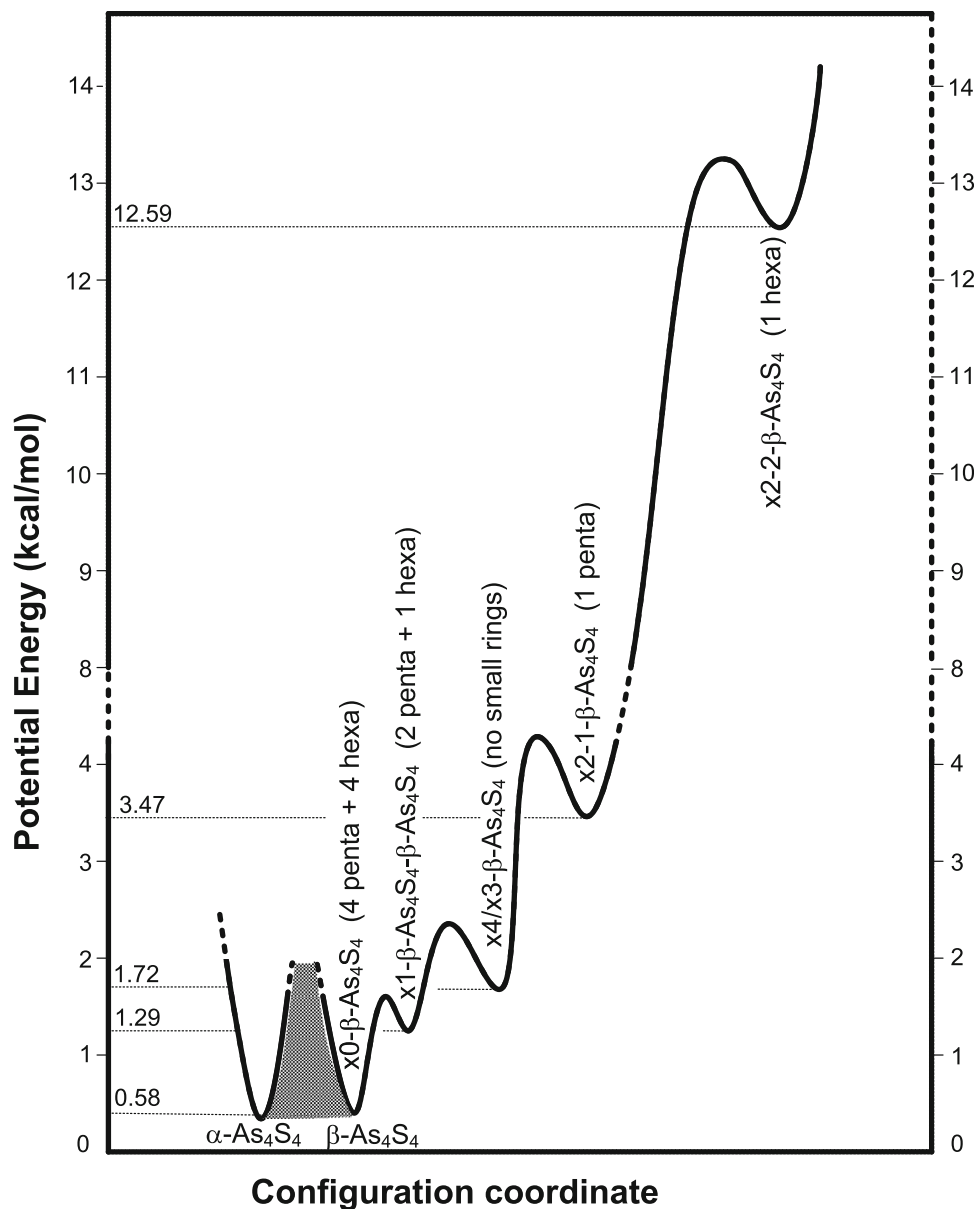
Pararealgar  $\text{As}_4\text{S}_4$  as metastable product of light-induced alteration from both tetra-arsenic tetrasulphide polymorphs ( $\alpha\text{-As}_4\text{S}_4$  and  $\beta\text{-As}_4\text{S}_4$ ) [8, 41, 42], was found to exist (albeit in small amount) in  $\text{As}_4\text{S}_4\text{-As}_4\text{S}_3$  alloys prepared by melt-quenching and/or nanomilling [20] (following the Kyono's notation [43], and for sake of convenience, this phase will be marked thereafter as p- $\text{As}_4\text{S}_4$ ).

Notwithstanding, the network-forming tendencies derived from this pararealgar p- $\text{As}_4\text{S}_4$  phase should be accepted in the overall balance of possible amorphization scenarios in the studied arsenicals, provided they were preliminary light-soaked.

The simulated pararealgar-type p- $\text{As}_4\text{S}_4$  cage-like molecule possesses reduced  $C_s$  symmetry due to asymmetric adjacent configuration of two neighboring homonuclear As-As bonds (such as As4-As3 and As2-As3 on Fig. 3a) with common As3 atom, the optimized parameters of this configuration in Table 2 being agreed with those determined from the known experimental model [40]. This p- $\text{As}_4\text{S}_4$  molecule includes one tetragon ( $\text{As}_2\text{As}_3\text{As}_4\text{S}_1$ ), two pentagons ( $\text{As}_1\text{S}_2\text{As}_2\text{As}_3\text{S}_3$  and  $\text{As}_1\text{S}_4\text{As}_4\text{As}_3\text{S}_3$ ) and one hexagon ( $\text{As}_1\text{S}_4\text{As}_4\text{S}_1\text{As}_2\text{S}_2$ ), thus resulting in under-constrained topological motive with  $n_c = 2.75$  (Table 3). In comparison with realgar-type  $\text{As}_4\text{S}_4$  molecule (Fig. 1a), the calculated  $E_f$  energy for this molecule is higher approaching - 0.94 kcal/mol.

A great variety of network-forming clusters are expected from this asymmetric configuration of metastable p- $\text{As}_4\text{S}_4$  molecule, their small-ring characteristics (number and type of small rings, hexagons/pentagons/tetragons) and cluster-forming energies  $E_f$  being presented in Table 3. The most plausible among them seems to be  $\times$  4-p- $\text{As}_4\text{S}_4$  cluster reconstructed from  $\text{As}_4\text{S}_8\text{H}_8$  molecular precursor due to quadruple  $\times$  4-break in all S atom positions, which completely destroys small-ring structure of this molecule separating arsenical matrix on  $\text{AsS}_3\text{H}_3$  and  $\text{As}_3\text{S}_5\text{H}_5$  molecular precursors (see Fig. 3b). From network-reconstruction viewpoint, this cluster with equivalent bond distances and angles given in Table 4 results in over-constrained topology of overall backbone with  $n_c = 3.25$  in average. Realistically, this configuration split into amorphous sub-networks composed of optimally-constrained interlinked  $\text{AsS}_{3/2}$  pyramids ( $Z = 2.40$ ;  $n_c = 3.00$ ) and over-constrained stressed-rigid  $\text{As}_3\text{S}_{5/2}$  chains ( $Z = 2.55$ ;  $n_c = 3.36$ ). Direct bonded As-S and As-As distances in these clusters fit respectively within  $\sim 2.26$  Å and  $\sim 2.47$  Å, while

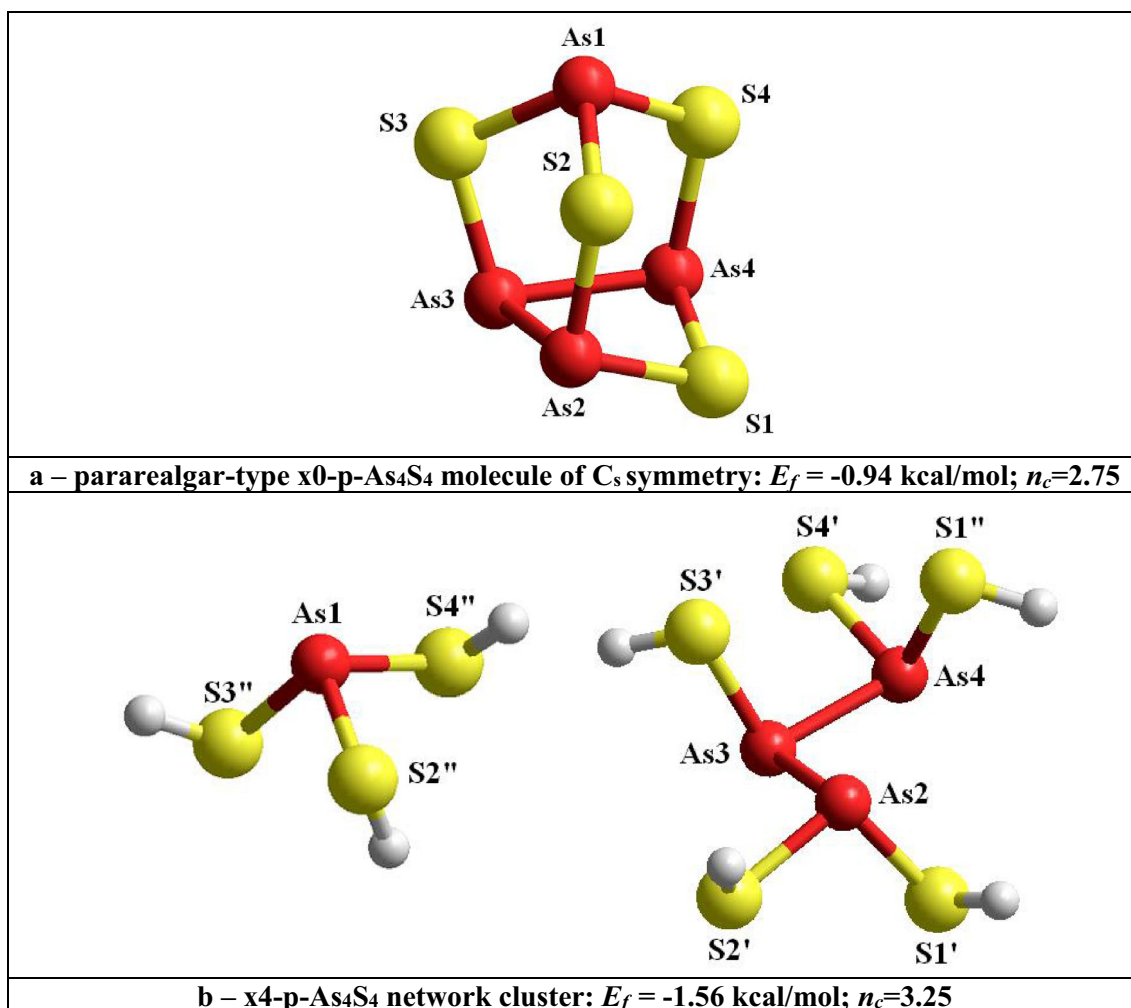
**Fig. 2** Potential energy landscape showing amorphization scenarios derived from  $\beta$ -As<sub>4</sub>S<sub>4</sub> phase. The settle-points corresponding to network clusters derived from realgar-type As<sub>4</sub>S<sub>4</sub> molecules by  $x$ -fold bond-breaking (keeping small rings, such as pentagons/hexagons nominated in parenthesis) are denoted with respective cluster-forming energies  $E_f$  at the right axis. The ground molecular-crystalline state is given in double-well presentation for low-temperature realgar  $\alpha$ -As<sub>4</sub>S<sub>4</sub> and high-temperature  $\beta$ -As<sub>4</sub>S<sub>4</sub> polymorph (no amorphization transitions are expected from  $\alpha$ -As<sub>4</sub>S<sub>4</sub> state)



more essential deviations are observed in bond angles at As atoms. Molecular-to-network barrier for this amorphization pathway is low approaching  $\Delta E_f = (1.56-0.94)$  kcal/mol = 0.62 kcal/mol, this value being comparable with  $\Delta E_f$  for other transitions forming optimally-constrained single-broken  $\times 1-1-p$ -As<sub>4</sub>S<sub>4</sub> ( $\Delta E_f = 0.84$  kcal/mol) and triple-broken  $\times 3-1-p$ -As<sub>4</sub>S<sub>4</sub> derivatives ( $\Delta E_f = 1.19$  kcal/mol) having  $n_c = 3.00$ , along with over-constrained double-broken  $\times 2-4-p$ -As<sub>4</sub>S<sub>4</sub> derivatives with  $n_c = 3.25$  ( $\Delta E_f = 1.15$  kcal/mol). These data testify in favor of rather shallow-level character of respective potential energy landscape on Fig. 4 illustrating amorphization scenarios originated from pararealgar-type p-As<sub>4</sub>S<sub>4</sub> arsenicals. Because of low barriers between these wells, transition towards quadruple-broken  $\times 4-p$ -As<sub>4</sub>S<sub>4</sub> network-forming

clusters possessing  $E_f = -1.56$  kcal/mol seems to be most favorable.

Thus, decomposition on two different topological sub-networks occurs first from p-As<sub>4</sub>S<sub>4</sub> arsenical, these being *stoichiometric* optimally-constrained ( $Z = 2.40$ ,  $n_c = 3.00$ ) and *non-stoichiometric* As-rich over-constrained ones ( $Z = 2.55$ ,  $n_c = 3.36$ ). In the realistic arsenical systems compositionally close to arsenic monosulphide AsS, this process is expected to be merely blocked, provided appearance of pararealgar p-As<sub>4</sub>S<sub>4</sub> phase is inhibited.



**Fig. 3** Geometrically-optimized configurations of pararealgar-type p-As<sub>4</sub>S<sub>4</sub> cage-like molecule (**a**) and its most energetically favorable network derivative separating arsenical matrix on AsS<sub>3</sub>H<sub>3</sub> and As<sub>3</sub>S<sub>5</sub>H<sub>5</sub> molecules due to quadruple  $\times 4$ -break in S1-S2-S3-S4

positions. The terminated H atoms are grey colored, S and As atoms are respectively depicted by yellow and red balls, and covalent bonds between atoms are stick-denoted

### Cluster Modeling of Amorphization Paths Derived from Dimorphite $\alpha/\beta$ -As<sub>4</sub>S<sub>3</sub> Phases

Removing one S atom at the bottom of pararealgar p-As<sub>4</sub>S<sub>4</sub> molecule (within As2-As3-As4-S1 sequence, Fig. 3a), replacing it by one As-As bond, transfers this molecule to other one As<sub>4</sub>S<sub>3</sub>-I corresponding to both low- and high-temperature polymorphs of mineral dimorphite  $\alpha/\beta$ -As<sub>4</sub>S<sub>3</sub> [12, 13]. This is most energetically plausible configuration of this As<sub>4</sub>S<sub>3</sub> molecule formed from six heteronuclear As-S and three homonuclear As-As bonds as shown on Fig. 5a. The optimized bond distances and angles in this  $\times 0$ -As<sub>4</sub>S<sub>3</sub>-I molecule obeying *triangle-like* conformation due to the basal 3-membered As<sub>3</sub>-ring (triangle) composed of As2-As3-As4 atoms, surmounted by AsS<sub>3/2</sub> pyramid composed of As1-(S1-S2-S3) atoms (see Fig. 5a) have been derived from CINCA modeling and gathered in

Table 5. It's seen that direct bonded As-As distances in As<sub>3</sub>-triangle approach  $\sim 2.467$  Å with all bond angles close to  $\sim 60^\circ$ . Direct bonded As-S distances within AsS<sub>3/2</sub> pyramid and As-S distances connecting this pyramid with bottom As<sub>3</sub>-ring approach  $\sim 2.235$  Å, with angle on As1 atom at the apex of AsS<sub>3/2</sub> pyramid close to  $\sim 99.04^\circ$ . The calculated  $E_f$  energy for this molecule (in respect to the energy of AsS<sub>3/2</sub> pyramid) was found to be  $-1.78$  kcal/mol (see Table 6), the value worse than in molecular As<sub>4</sub>S<sub>4</sub>-type polymorphs, but comparable and even better than in network-forming derivatives from these cage-like molecules (compare respective energies in Tables 1, 3, 6).

Previously, the crystallographic features of under-constrained As<sub>4</sub>S<sub>3</sub> molecule ( $n_c = 2.71$ , Table 6) possessing C<sub>3v</sub> symmetry with four small rings (three pentagons and one triangle) were specified (see, e.g. refs. [8, 14]), and geometrically-optimized parameters of this molecule were

**Table 2** Geometrically-optimized bond distances and angles in pararealgar-type p-As<sub>4</sub>S<sub>4</sub> molecule (atom labels refer to Fig. 3a)

Equivalent bond distances		Equivalent bond angles			
Atoms	Distance (Å)	Atoms	Distance (Å)	Angle	Deg. (°)
<i>Direct bonded distances</i>				∠ S–As–S	
As3–As4	2.4898	As2–As3	2.4905	∠ S1–As4–S4	104.406
As1–S2	2.2453	As2–S1	2.2652	∠ S1–As2–S2	104.398
As1–S3	2.2486	As2–S2	2.2487	∠ S2–As1–S4	104.239
As1–S4	2.2460	As4–S1	2.2652	∠ S2–As1–S3	98.843
As3–S3	2.2141	As4–S4	2.2486	∠ S3–As1–S4	98.783
<i>Non-bonded distances</i>				∠ S–As–As	
As1–As2	3.6481	As1–As4	3.6487	∠ S3–As3–As2	101.756
As1–As3	3.4837	As2–As4	3.3508	∠ S3–As3–As4	101.754
				∠ S2–As2–As3	100.465
As1–S1	4.3673	As3–S2	3.6460	∠ S4–As4–As3	100.457
As2–S3	3.6540	As3–S4	3.6452	∠ S1–As2–As3	86.002
As2–S4	4.1150	As4–S2	4.1154	∠ S1–As4–As3	86.019
As3–S1	3.2476	As4–S3	3.6533	∠ As–As–As	
				∠ As2–As3–As4	84.570
S1–S2	3.5668	S2–S3	3.4132	∠ As–S–As	
S1–S3	4.7549	S2–S4	3.5449	∠ As2–S2–As1	108.539
S1–S4	3.5666	S3–S4	3.4122	∠ As4–S4–As1	108.543
				∠ As3–S3–As1	102.635
				∠ As2–S1–As4	95.398

**Table 3** Cluster-forming energies  $E_f$  (in respect to the energy of AsS<sub>3/2</sub> pyramid) for network-forming derivatives from pararealgar-type p-As<sub>4</sub>S<sub>4</sub> molecule (atom labels refer to Fig. 3a)

Molecular prototype	Network/molecular cluster, and respective cluster-forming path	Number of rings: hexagons/pentagons/tetragons	$n_c$	$E_f$ (kcal/mol)
p-As <sub>4</sub> S <sub>4</sub>	× 0-p-As <sub>4</sub> S <sub>4</sub> , no break (× 0-break)	1/2/1	2.75	– 0.94
As <sub>4</sub> S <sub>5</sub> H <sub>2</sub>	× 1–1-p-As <sub>4</sub> S <sub>4</sub> , × 1-break in S1	0/2/0	3.00	– 1.78
As <sub>4</sub> S <sub>5</sub> H <sub>2</sub>	× 1–2-p-As <sub>4</sub> S <sub>4</sub> , × 1-break in S2	0/1/1	2.875	– 3.01
As <sub>4</sub> S <sub>5</sub> H <sub>2</sub>	× 1–3-p-As <sub>4</sub> S <sub>4</sub> , × 1-break in S3	1/0/1	3.00	– 3.09
As <sub>4</sub> S <sub>6</sub> H <sub>4</sub>	× 2–1-p-As <sub>4</sub> S <sub>4</sub> , × 2-break in S2–S4	0/0/1	3.00	– 4.82
As <sub>4</sub> S <sub>6</sub> H <sub>4</sub>	× 2–2-p-As <sub>4</sub> S <sub>4</sub> , × 2-break in S2–S1	0/1/0	3.125	– 8.41
As <sub>4</sub> S <sub>6</sub> H <sub>4</sub>	× 2–3-p-As <sub>4</sub> S <sub>4</sub> , × 2-break in S2–S3	0/0/1	3.00	– 12.12
As <sub>4</sub> S <sub>6</sub> H <sub>4</sub>	× 2–4-p-As <sub>4</sub> S <sub>4</sub> , × 2-break in S3–S1	1/0/0	3.25	– 2.09
As <sub>4</sub> S <sub>7</sub> H <sub>6</sub>	× 3–1-p-As <sub>4</sub> S <sub>4</sub> , × 3-break in S2–S4–S3	0/0/1	3.00	– 2.13
As <sub>4</sub> S <sub>7</sub> H <sub>6</sub>	× 3–2-p-As <sub>4</sub> S <sub>4</sub> , × 3-break in S2–S4–S1	0/0/0	3.25	– 7.98
As <sub>4</sub> S <sub>7</sub> H <sub>6</sub>	× 3–3-p-As <sub>4</sub> S <sub>4</sub> , × 3-break in S2–S3–S1	0/0/0	3.25	– 7.14
As <sub>4</sub> S <sub>8</sub> H <sub>8</sub>	× 4-p-As <sub>4</sub> S <sub>4</sub> , × 4-break in S1–S2–S3–S4	0/0/0	3.25	– 1.56

derived from *ab-initio* quantum-chemical model of Kyono [43]. However, the energetic specificity of competitive molecular-network amorphizing tendencies in dimorphite-type As<sub>4</sub>S<sub>3</sub> arsenicals has not been established.

In general, dimorphite  $\alpha/\beta$ -As<sub>4</sub>S<sub>3</sub>-type molecule allows three network-forming configurations, which can be reconstructed from × 0-As<sub>4</sub>S<sub>3</sub>-I cages shown on Fig. 5a

by × 1-, × 2-, × 3-breaking in respective S1, S2, S3 positions, these configurations being parameterized and compared in Table 6.

The optimally-constrained double-broken × 2-As<sub>4</sub>S<sub>3</sub>-I clusters having  $n_c = 3.00$  in view of one small ring kept in the structure (As<sub>3</sub>-triangle) cannot be stabilized in realistic amorphous structures because of unfavorable cluster-

**Table 4** Geometrically-optimized bond distances and angles in network derivative from pararealgar-type p-As<sub>4</sub>S<sub>4</sub> cage-like molecule separating matrix on AsS<sub>3</sub>H<sub>3</sub> and As<sub>3</sub>S<sub>5</sub>H<sub>5</sub> molecules due to quadruple × 4-break in all S atoms (atom labels refer to Fig. 3b)

Equivalent bond distances				Equivalent bond angles	
Atoms	Distance (Å)	Atoms	Distance (Å)	Angle	Deg. (°)
AsS <sub>3</sub> H <sub>3</sub> molecule					
<i>Direct bonded distances</i>					
As1–S2''	2.2540	As1–S4''	2.2561	∠ S–As–S	
As1–S3''	2.2515			∠ S4''–As1–S2''	101.939
<i>Non-bonded distances</i>					
S2''–S3''	3.5246	S3''–S4''	3.2608	∠ S4''–As1–S3''	92.673
S2''–S4''	3.5035			∠ S2''–As1–S3''	102.941
As <sub>3</sub> S <sub>5</sub> H <sub>5</sub> molecule					
<i>Direct bonded distances</i>					
As3–As4	2.4730	As2–As3	2.4659	∠ S–As–S	
As2–S1'	2.2605	As4–S1''	2.2595	∠ S1''–As4–S4'	101.787
As2–S2'	2.2611	As4–S4'	2.2525	∠ S1'–As2–S2'	101.412
As3–S3'	2.2573			∠ S–As–As	
<i>Non-bonded distances</i>					
As2–As4	3.7602	S1'–S1''	4.7220	∠ S1'–As2–As3	94.938
As2–S1''	3.9534	S1'–S2'	3.4992	∠ S2'–As2–As3	95.462
As2–S3'	3.4688	S1'–S3'	5.3008	∠ S3'–As3–As2	94.414
As2–S4'	5.4982	S1'–S4'	6.0459	∠ S3'–As3–As4	102.986
As3–S1'	3.4856	S2'–S1''	6.0918	∠ S1''–As4–As3	103.109
As3–S1''	3.7089	S2'–S3'	4.2681	∠ S4'–As4–As3	94.737
As3–S2'	3.5006	S2'–S4'	6.9640	∠ As–As–As	
As3–S4'	3.4799	S3'–S1''	3.8688	∠ As2–As3–As4	99.165
As4–S1'	3.9519	S3'–S4'	3.8463		
As4–S2'	5.5827	S4'–S1''	3.5012		
As4–S3'	3.7041				

forming energy  $E_f = -11.68$  kcal/mol (Table 6). The most plausible amorphization path originated from this  $\alpha/\beta$ -As<sub>4</sub>S<sub>3</sub>-type arsenical seems to be related to other possibility of molecular-cage destroying connected with × 3-break in all S atom positions, when arsenical matrix built of × 3-As<sub>4</sub>S<sub>3</sub>-I clusters ( $Z = 2.57$ ;  $n_c = 3.00$ ) are decomposed in two optimally-constrained sub-networks having AsS<sub>3</sub>H<sub>3</sub> and As<sub>3</sub>S<sub>3</sub>H<sub>3</sub> molecular precursors (Fig. 5c). Like in pararealgar structures, one sub-network is composed of AsS<sub>3/2</sub> pyramids ( $Z = 2.40$ ;  $n_c = 3.00$ ) with identical parameters (compare these parameters for AsS<sub>3</sub>H<sub>3</sub> molecule separated from p-As<sub>4</sub>S<sub>4</sub> in Table 4 and from  $\alpha/\beta$ -As<sub>4</sub>S<sub>3</sub> in Table 7). Other sub-network decomposed from dimorphite-type arsenicals under × 3-break represents optimally-constrained As<sub>3</sub>S<sub>3/2</sub> clusters ( $Z = 2.67$ ;  $n_c = 3.00$ ) keeping basal As<sub>3</sub>-ring incorporated by triplicate = As–S–chain links. As it follows from potential energy landscape on Fig. 6a, the calculated molecular-to-network barrier for this amorphization path is low  $\Delta E_f = (3.96-1.78)$  kcal/mol = 2.18 kcal/mol. The only competitive variant for this amorphization scenario in dimorphite-type arsenicals is incomplete destroying of As<sub>4</sub>S<sub>3</sub>-I molecule in *triangle-like*

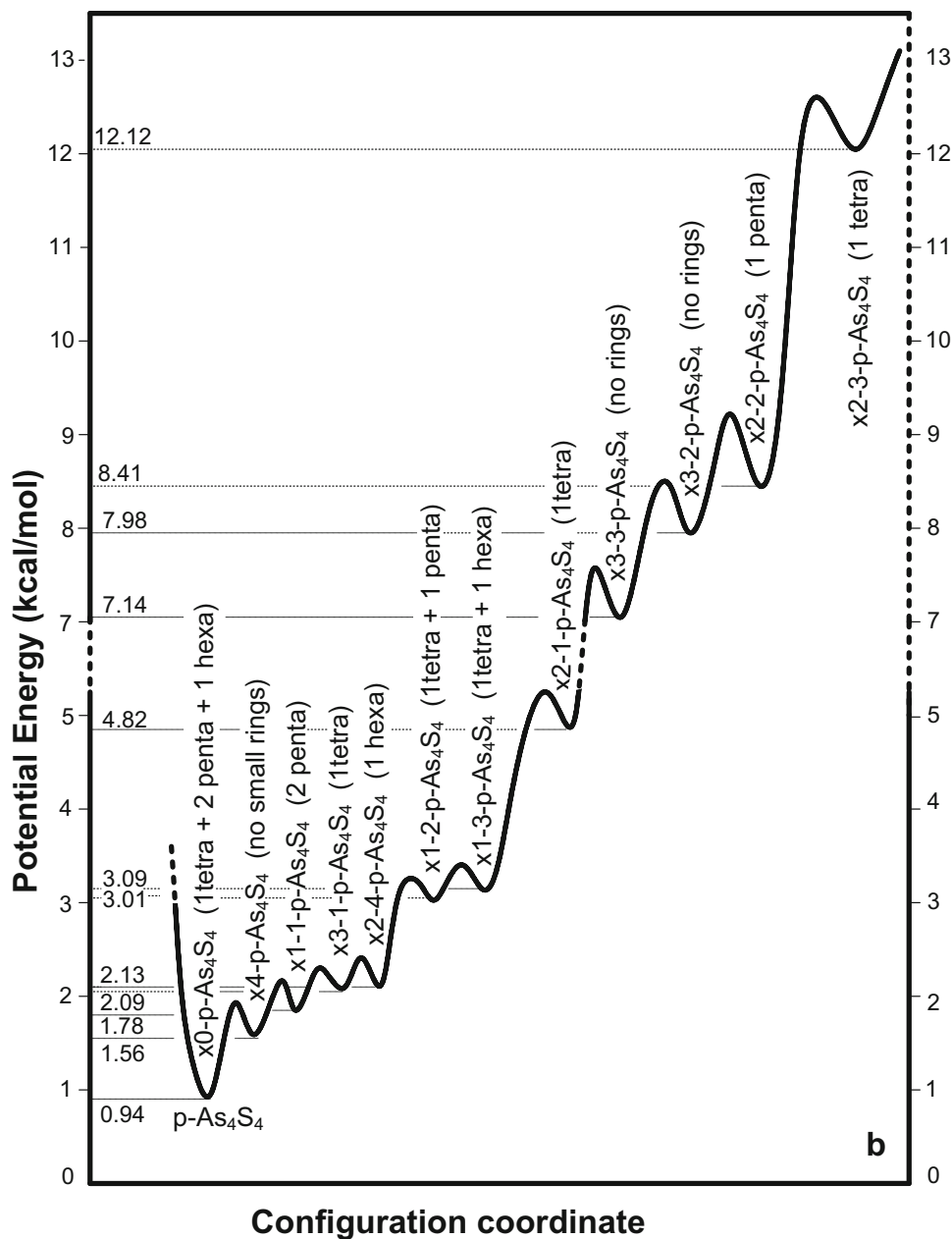
conformation due to × 1-break in S1 position keeping two neighboring small rings (triangle As<sub>2</sub>As<sub>3</sub>As<sub>4</sub> and pentagon As<sub>2</sub>As<sub>4</sub>S<sub>3</sub>As<sub>1</sub>S<sub>1</sub>, see Fig. 5b), thus stabilizing under-constrained amorphous matrix with  $n_c = 2.86$  and comparable value of  $E_f = -4.24$  kcal/mol.

The *triangle-like* conformation shown in Fig. 5a is not alone arrangement of As<sub>4</sub>S<sub>3</sub> molecular cages, two other under-constrained configurations, the *chain-like* As<sub>4</sub>S<sub>3</sub>-II with  $n_c = 2.71$  (Fig. 7a) and *star-like* As<sub>4</sub>S<sub>3</sub>-III with  $n_c = 2.57$  (Fig. 8a), being also possible. The optimized geometrical parameters for these molecules were simulated by Kyono [43], however, this author was failed to distinguish energetically realistic configurations among these As<sub>4</sub>S<sub>3</sub>-type arsenicals.

Removing S atom from one of two equivalent positions S2 or S4 within asymmetric p-As<sub>4</sub>S<sub>4</sub> molecule on Fig. 3a, replacing it by As–As bond, transfers this molecule to other one As<sub>4</sub>S<sub>3</sub>-II distinguished by *chain-like* or *zig-zag* conformation due to sequent arrangement of all four As atoms (within As<sub>1</sub>As<sub>3</sub>As<sub>2</sub>As<sub>4</sub> chain as shown in Fig. 7a). The cluster-forming  $E_f$  energies for geometrically-optimized configuration of this molecule and its main network-



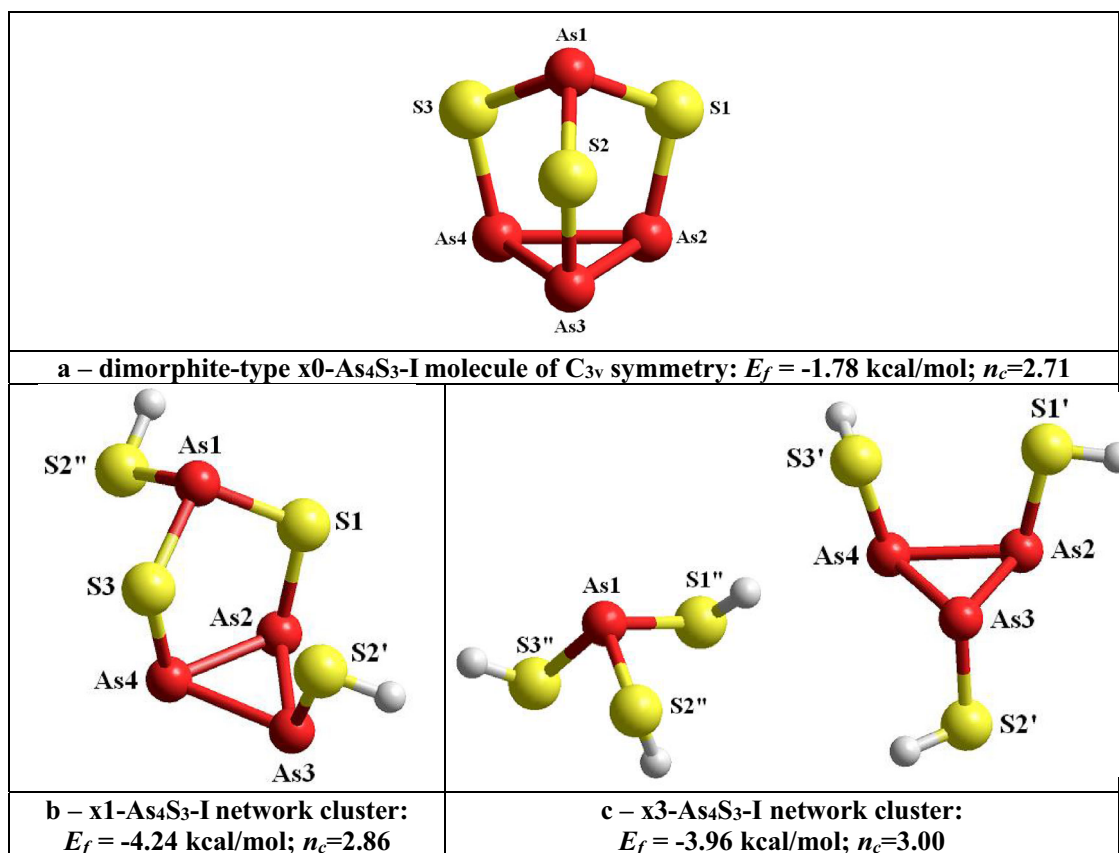
**Fig. 4** Potential energy landscape illustrating amorphization scenarios derived from pararealgar-type  $p\text{-As}_4\text{S}_4$  arsenical. The shallow-level character of network-forming derivatives reconstructed from pararealgar  $\times 0\text{-}p\text{-As}_4\text{S}_4$  molecule is obvious. The settle-points of network clusters derived by  $x$ -fold bond-breaking (keeping small rings, such as tetragons/pentagons/hexagons nominated in parenthesis) are denoted with respective cluster-forming energies  $E_f$  at the right axis



forming derivatives are gathered in Table 6 and reflected on potential energy landscape (see Fig. 6b). It's clearly seen that two types of network derivatives (single-broken  $\times 1\text{-}1\text{-As}_4\text{S}_3\text{-II}$  with  $n_c = 3.00$  and triple-broken  $\times 3\text{-As}_4\text{S}_3\text{-II}$  with  $n_c = 3.43$ ) are more favorable than parent  $\times 0\text{-As}_4\text{S}_3\text{-II}$  molecule, the configuration of optimally-constrained  $\times 1\text{-}1\text{-As}_4\text{S}_3\text{-II}$  network cluster being shown on Fig. 7b. It means that this *chain-like* molecular conformation cannot be stabilized realistically, being rather defective one.

The similar finding concerns other conformation possible for molecular  $\text{As}_4\text{S}_3$  cages on Fig. 8a. This is so-called *star-like* conformation of  $\times 0\text{-As}_4\text{S}_3\text{-III}$  molecule, which

can be reconstructed from pararealgar  $p\text{-As}_4\text{S}_4$  molecule (Fig. 3a) removing S atom from S3 position of surmounted pyramid  $\text{As1(S2S3S4)}$ . The character *star-like* configuration in this molecule is formed by central As4 atom bonded to other three As atoms (As1, As2, and As3) as illustrated on Fig. 8a. As it follows from potential energy landscape on Fig. 6c, this under-constrained  $\times 0\text{-As}_4\text{S}_3\text{-III}$  molecule ( $n_c = 2.57$ ) is evidently unfavorable before two over-constrained network derivatives such as double-broken  $\times 2\text{-As}_4\text{S}_3\text{-III}$  with  $n_c = 3.14$  (Fig. 8b) and triple-broken  $\times 3\text{-As}_4\text{S}_3\text{-III}$  with  $n_c = 3.43$ . Therefore, as in the previous case, the *star-like* conformation is not expected in realistic  $\text{As}_4\text{S}_3$ -type arsenical structures.



**Fig. 5** Geometrically-optimized configurations of dimorphite-type  $\alpha/\beta$ -As<sub>4</sub>S<sub>3</sub> cage-like molecule in *triangle-like* conformation  $\times 0$ -As<sub>4</sub>S<sub>3</sub>-I (a) and its most energetically favorable network derivatives formed from As<sub>4</sub>S<sub>4</sub>H<sub>2</sub> molecule by single  $\times 1$ -break in S2 position (b) and

separating matrix on AsS<sub>3</sub>H<sub>3</sub> and As<sub>3</sub>S<sub>3</sub>H<sub>3</sub> molecules due to triple  $\times 3$ -break in S1-S2-S3 positions (c). The terminated H atoms are grey-colored, S and As atoms are yellow- and red-depicted, and covalent bonds between atoms are stick-denoted

**Table 5** Geometrically-optimized bond distances and angles in dimorphite-type  $\alpha/\beta$ -As<sub>4</sub>S<sub>3</sub> cage-like molecule (atom labels refer to Fig. 5a)

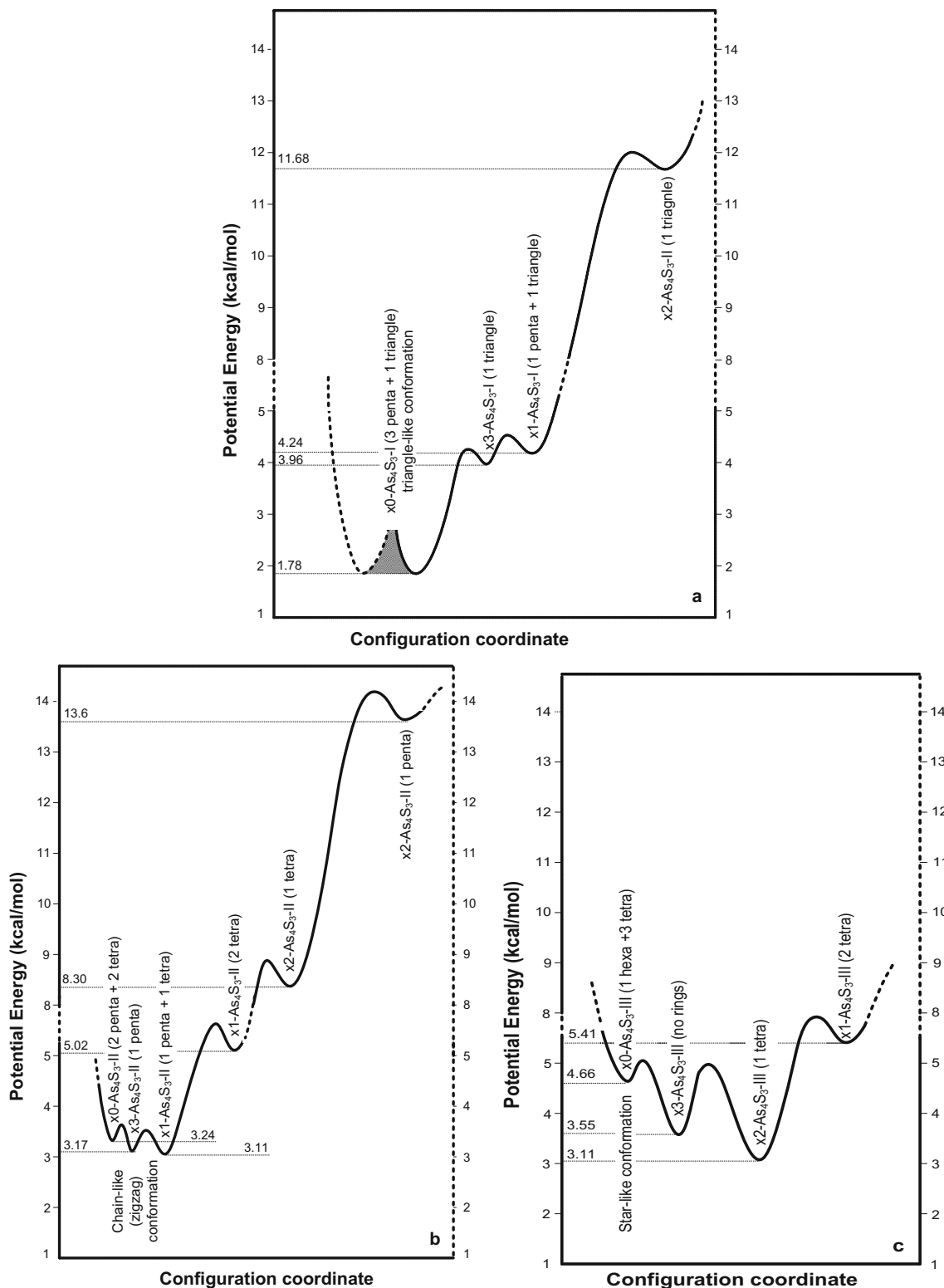
Equivalent bond distances				Equivalent bond angles				
Atoms	Distance (Å)	Atoms	Distance (Å)	Angle	Deg. (°)	Angle	Deg. (°)	
<i>Direct bonded distances</i>				$\angle S-As-S$		$\angle As-S-As$		
As2-As3	2.4668	As3-As4	2.4664	$\angle S1-As1-S2$	99.042	$\angle As1-S1-As2$	104.627	
As2-As4	2.4668			$\angle S1-As1-S3$	99.040	$\angle As1-S2-As3$	104.596	
As1-S1	2.2349	As2-S1	2.2348	$\angle S2-As1-S3$	99.037	$\angle As1-S3-As4$	104.595	
As1-S2	2.2353	As3-S2	2.2349					
As1-S3	2.2352	As4-S3	2.2349	$\angle S-As-As$		$\angle As-As-As$		
<i>Non-bonded distances</i>				$\angle S1-As2-As3$		102.039	$\angle As3-As2-As4$	59.990
As1-As2	3.5372	As1-As4	3.5368	$\angle S1-As2-As4$	102.038	$\angle As2-As3-As4$	60.005	
As1-As3	3.5368	As4-S1	3.6577	$\angle S2-As3-As2$	102.069	$\angle As2-As4-As3$	60.005	
As2-S2	3.6586	As4-S2	3.6580	$\angle S2-As3-As4$	102.058			
As2-S3	3.6586	S1-S2	3.4002	$\angle S3-As4-As2$	102.068			
As3-S1	3.6577	S1-S3	3.4001	$\angle S3-As4-As3$	102.062			
As3-S3	3.6581	S2-S3	3.4003					

**Table 6** Cluster-forming energies  $E_f$  (in respect to the energy of  $\text{AsS}_{3/2}$  pyramid) for network-forming derivatives from  $\text{As}_4\text{S}_3$ -type cage-like molecules (atom labels refer to Fig. 5a, 7a, 8a)

Molecular prototype	Network/molecular cluster, and respective cluster-forming path	Number of rings: pentagons/tetragons/triangles	$n_c$	$E_f$ (kcal/mol)
Dimorphite-type $\alpha/\beta$ - $\text{As}_4\text{S}_3$ cage-like molecule in <i>triangle-like</i> conformation				
$\text{As}_4\text{S}_3\text{-I}$	$\times$ 0- $\text{As}_4\text{S}_3\text{-I}$ , no breaks	3/0/1	2.71	- 1.78
$\text{As}_4\text{S}_4\text{H}_2$	$\times$ 1- $\text{As}_4\text{S}_3\text{-I}$ , $\times$ 1-break in S1	1/0/1	2.86	- 4.24
$\text{As}_4\text{S}_5\text{H}_4$	$\times$ 2- $\text{As}_4\text{S}_3\text{-I}$ , $\times$ 2-break in S1-S2	0/0/1	3.00	- 11.68
$\text{As}_4\text{S}_6\text{H}_6$	$\times$ 3- $\text{As}_4\text{S}_3\text{-I}$ , $\times$ 3-break in S1-S2-S3	0/0/1	3.00	- 3.96
$\text{As}_4\text{S}_3$ cage-like molecule in <i>chain-like</i> conformation				
$\text{As}_4\text{S}_3\text{-II}$	$\times$ 0- $\text{As}_4\text{S}_3\text{-II}$ , no breaks	2/2/0	2.71	- 3.23
$\text{As}_4\text{S}_4\text{H}_2$	$\times$ 1-1- $\text{As}_4\text{S}_3\text{-II}$ , $\times$ 1-break in S2	1/1/0	3.00	- 3.11
$\text{As}_4\text{S}_4\text{H}_2$	$\times$ 1-2- $\text{As}_4\text{S}_3\text{-II}$ , $\times$ 1-break in S1	0/2/0	2.86	- 5.02
$\text{As}_4\text{S}_5\text{H}_4$	$\times$ 2-1- $\text{As}_4\text{S}_3\text{-I}$ , $\times$ 2-break in S2-S3	1/0/0	3.29	- 13.60
$\text{As}_4\text{S}_5\text{H}_4$	$\times$ 2-2- $\text{As}_4\text{S}_3\text{-I}$ , $\times$ 2-break in S1-S3	0/1/0	3.14	- 8.30
$\text{As}_4\text{S}_6\text{H}_6$	$\times$ 3- $\text{As}_4\text{S}_3\text{-II}$ , $\times$ 3-break in S1-S2-S3	0/0/0	3.43	- 3.17
$\text{As}_4\text{S}_3$ cage-like molecule in <i>star-like</i> conformation				
$\text{As}_4\text{S}_3\text{-III}$	$\times$ 0- $\text{As}_4\text{S}_3\text{-III}$ , no breaks	0/3/0	2.86	- 4.66
$\text{As}_4\text{S}_4\text{H}_2$	$\times$ 1- $\text{As}_4\text{S}_3\text{-III}$ , $\times$ 1-break in S1	0/2/0	2.86	- 5.41
$\text{As}_4\text{S}_5\text{H}_4$	$\times$ 2- $\text{As}_4\text{S}_3\text{-III}$ , $\times$ 2-break in S1-S2	0/1/0	3.14	- 3.11
$\text{As}_4\text{S}_6\text{H}_6$	$\times$ 3- $\text{As}_4\text{S}_3\text{-III}$ , $\times$ 3-break in S1-S2-S3	0/0/0	3.43	- 3.55

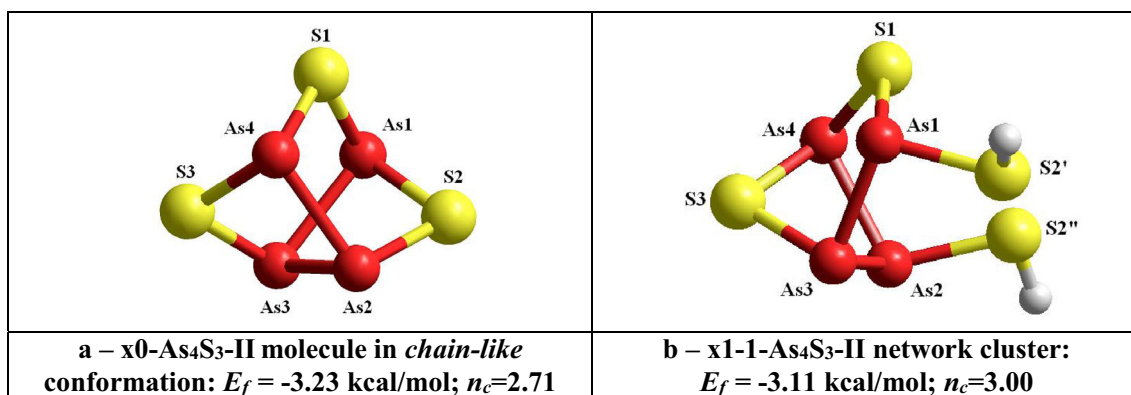
**Table 7** Geometrically-optimized bond distances and angles in network derivative from dimorphite  $\alpha/\beta$ - $\text{As}_4\text{S}_3$  cage-like molecule in *triangle-like* conformation, separating matrix on  $\text{AsS}_3\text{H}_3$  and  $\text{As}_3\text{S}_3\text{H}_3$  molecules due to triple  $\times$  3-break in S1-S2-S3 positions (atom labels refer to Fig. 5c)

Equivalent bond distances				Equivalent bond angles	
Atoms	Distance (Å)	Atoms	Distance (Å)	Angle	Deg. (°)
<b><math>\text{AsS}_3\text{H}_3</math> molecule</b>					
<i>Direct bonded distances</i>					
As1-S2''	2.2540	As1-S4''	2.2561	$\angle$ S-As-S	
As1-S3''	2.2515			$\angle$ S4''-As1-S2''	101.939
				$\angle$ S4''-As1-S3''	92.673
<i>Non-bonded distances</i>					
S2''-S3''	3.5246	S3''-S4''	3.2608	$\angle$ S2''-As1-S3''	102.941
S2''-S4''	3.5035				
<b><math>\text{As}_3\text{S}_3\text{H}_3</math> molecule</b>					
<i>Direct bonded distances</i>					
As2-As3	2.4500	As3-As4	2.4589	$\angle$ As-As-As	
As2-As4	2.4728	As3-S2'	2.2724	$\angle$ As3-As2-As4	59.931
As2-S1'	2.2600	As4-S3'	2.2631	$\angle$ As2-As3-As4	60.496
				$\angle$ As2-As4-As3	59.573
<i>Non-bonded distances</i>					
As2-S2'	3.4745	As4-S1'	3.7033	$\angle$ S-As-As	
As2-S3'	3.7687	As4-S2'	3.5417	$\angle$ S1'-As2-As3	99.979
				$\angle$ S1'-As2-As4	102.882
				$\angle$ S2'-As3-As2	94.668
As3-S1'	3.6095			$\angle$ S2'-As3-As4	96.853
As3-S3'	3.5565			$\angle$ S3'-As4-As2	105.370
				$\angle$ S3'-As4-As3	97.649



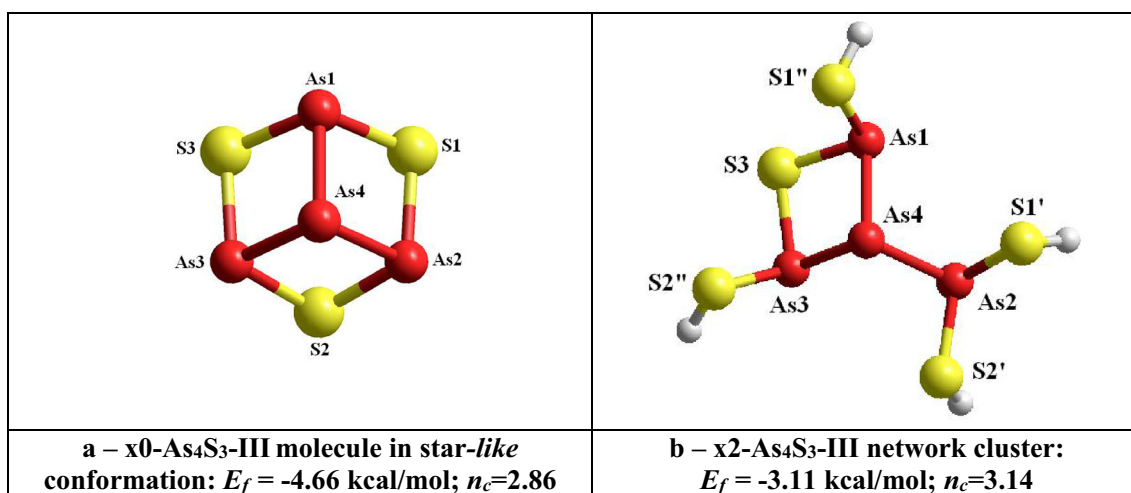
**Fig. 6** Potential energy landscapes showing diversity of amorphizing network-forming states originated from  $As_4S_3$  cage-like molecules in different conformations: *triangle-like* (a), *chain-like* or *zig-zag* (b), and *star-like* (c). The double-well presentation of ground state for *triangle-like*  $As_4S_3$ -I molecule corresponds to low- and high-

temperature modifications of tetra-arsenic trisulphide after Whitfield [12, 13]. The settle-points corresponding to network clusters derived by  $x$ -fold bond-breaking (keeping small rings, such as triangles/tetragons/pentagons/hexagons nominated in parenthesis) are denoted with respective forming energies  $E_f$  at the left axis



**Fig. 7** Geometrically-optimized configuration of As<sub>4</sub>S<sub>3</sub> cage molecule in *chain-like* conformation  $\times 0$ -As<sub>4</sub>S<sub>3</sub>-II (a) and its most favorable network derivative  $\times 1$ -1-As<sub>4</sub>S<sub>3</sub>-II formed from prototype

As<sub>4</sub>S<sub>4</sub>H<sub>2</sub> molecule by single  $\times 1$ -break in S2 position (b). The terminated H atoms are grey colored, S and As atoms are yellow- and red-depicted, and inter-cluster bonds are stick-denoted



**Fig. 8** Geometrically-optimized configuration of As<sub>4</sub>S<sub>3</sub> cage molecule in *star-like* conformation  $\times 0$ -As<sub>4</sub>S<sub>3</sub>-III (a) and its most favorable network derivative  $\times 2$ -As<sub>4</sub>S<sub>3</sub>-III formed from prototype

As<sub>4</sub>S<sub>5</sub>H<sub>4</sub> molecule by double  $\times 2$ -break in S1 and S2 positions (b). The terminated H atoms are grey colored, S and As atoms are yellow- and red-depicted, and inter-cluster bonds are stick-denoted

### Competitive Amorphization Scenarios in Nanostructured As<sub>4</sub>S<sub>4</sub>-As<sub>4</sub>S<sub>3</sub> Arsenicals

Recent calorimetric heat-capacity studies of nanoamorphization processes in As<sub>x</sub>S<sub>100-x</sub> arsenicals driven by external influences such as nanomilling testify that amorphous phase generated within As<sub>4</sub>S<sub>4</sub>-As<sub>4</sub>S<sub>3</sub> domain ( $2.50 < Z < 2.57$ ) is close to initial melt-quenched arsenical [20, 21, 40]. This fact assuredly serves as main argumentation on the appeared amorphous phase as mixture of network-forming derivatives originated from realgar As<sub>4</sub>S<sub>4</sub>-type and dimorphite As<sub>4</sub>S<sub>3</sub>-type molecules. Alternatively, this process can be classified as *nanomilling-driven amorphization* of melt-quenched alloy [19], in contrast to amorphization associated with decomposition of nanostructured phases occurring in these arsenicals enriched on plastic-crystalline  $\beta$ -As<sub>4</sub>S<sub>3</sub> phase [21].

Noteworthy, in respect to temperature-modulated DSC TOPEM® measurements [20, 39], amorphous nanophase generated in these arsenicals possesses double- $T_g$  relaxation, having high-temperature glass-transition mid-point  $T_{g1}$  close to that of melt-quenched As<sub>2</sub>S<sub>3</sub> alloy and low-temperature glass-transition mid-point  $T_{g2}$  near solidus of metastable melting in the respective over-stoichiometric arsenical.

Having in mind this specificity of calorimetric events in As<sub>x</sub>S<sub>100-x</sub> alloys, let's clarify diversity of amorphization scenarios realized in these arsenicals along As<sub>4</sub>S<sub>4</sub>-As<sub>4</sub>S<sub>3</sub> cut-line.

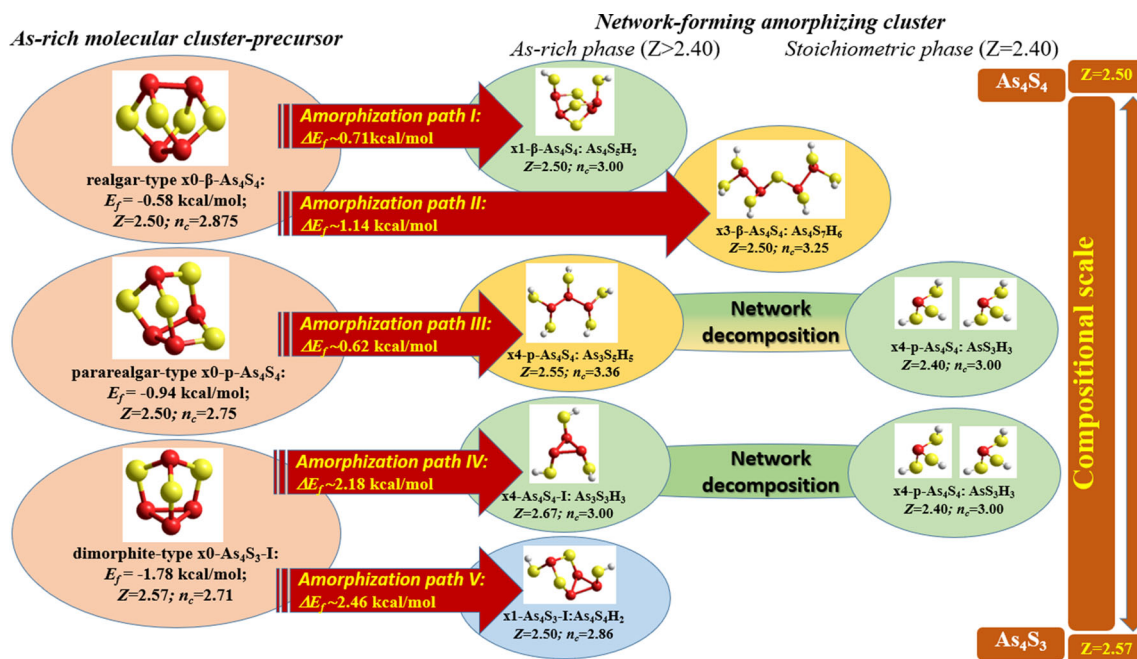
In realgar As<sub>4</sub>S<sub>4</sub>-type arsenicals with  $\times 0$ - $\beta$ -As<sub>4</sub>S<sub>4</sub> molecular cluster-precursor (see Fig. 1a), most energetically favorable network-forming amorphizing cluster  $\times 1$ - $\beta$ -As<sub>4</sub>S<sub>4</sub> can be derived from As<sub>4</sub>S<sub>5</sub>H<sub>2</sub> molecular precursor by single-break in one of S atom positions as illustrated in

Fig. 1b. This amorphization path I from molecular under-constrained arrangement ( $n_c = 2.875$ ) to network-forming optimally-constrained arrangement ( $n_c = 3.00$ ) keeping two pentagons is realized with the lowest inter-well barrier of  $\Delta E_f = 0.71$  kcal/mol (Fig. 9), thus being basic one for amorphizing  $\text{As}_4\text{S}_4$ -type arsenicals. Competitively, amorphization path II from  $\times 0$ - $\beta$ - $\text{As}_4\text{S}_4$  molecular precursor to over-constrained ( $n_c = 3.25$ ) triple-broken derivative (viz. chain-type  $\times 3$ - $\beta$ - $\text{As}_4\text{S}_4$  cluster) or, alternatively, but with smaller probability, to quadruple-broken derivative (viz.  $\times 4$ - $\beta$ - $\text{As}_4\text{S}_4$  or  $\text{As}_2\text{S}_{3/2}$  cluster) can be realized in this arsenical with barrier of  $\Delta E_f = 1.14$  kcal/mol. Whichever the case, these network-forming clusters ( $\times 1$ - $\beta$ - $\text{As}_4\text{S}_4$ ,  $\times 3$ - $\beta$ - $\text{As}_4\text{S}_4$  or  $\times 4$ - $\beta$ - $\text{As}_4\text{S}_4$ ) are over-stoichiometric ones ( $Z = 2.50$ ) contributing rather to network modes with low-temperature  $T_{g2}$  temperature near solidus of metastable melting in  $\text{As}_4\text{S}_4$  alloy.

The only variant on phase-decomposed amorphous substance which can be derived from  $\text{As}_4\text{S}_4$ -type alloys appears due to adjacent (neighboring) arrangement of both As-As bonds in pararealgar p- $\text{As}_4\text{S}_4$  structure (Fig. 3). Network decomposition occurs from p- $\text{As}_4\text{S}_4$  cage-like molecule (Fig. 3a) owing to  $\times 4$ -break in all S atom positions resulting in  $\times 4$ -p- $\text{As}_4\text{S}_4$  cluster, separating matrix on two sub-networks composed of optimally-constrained  $\text{AsS}_{3/2}$  pyramids ( $n_c = 3.00$ ,  $Z = 2.40$ ) and over-constrained  $\text{As}_3\text{S}_{5/2}$  chains ( $n_c = 3.36$ ,  $Z = 2.55$ ) with low

barrier of molecular-to-network transition approaching 0.62 kcal/mol, as depicted by amorphization pathway III on Fig. 9. Thus, the amorphous phase generated in this case possesses double- $T_g$  relaxation with high-temperature  $T_{g1}$  close to glass-transition mid-point of g- $\text{As}_2\text{S}_3$  ( $\sim 208$  °C [39]) and low-temperature  $T_{g2}$  near glass-transition mid-point corresponding to solidus of metastable melting of over-stoichiometric  $\text{As}_{55}\text{S}_{45}$  ( $\sim 130$  °C as determined by Hruby [1]). Realistically, such transformations in  $\text{As}_4\text{S}_4$ -type arsenicals are possible just from so-called  $\chi$ -phase  $\text{As}_4\text{S}_4$  considered as intermediate precursor of pararealgar p- $\text{As}_4\text{S}_4$  phase in light-induced alteration from  $\alpha/\beta$ - $\text{As}_4\text{S}_4$  phases [42, 44–46]. This  $\chi$ -phase  $\text{As}_4\text{S}_4$  was indeed identified in arsenic monosulphide employing the Raman scattering spectroscopy [20].

From the other side, in dimorphite  $\alpha/\beta$ - $\text{As}_4\text{S}_3$ -type arsenicals, amorphization can be realized only from  $\text{As}_4\text{S}_3$  molecules possessing *triangle-like* conformation of neighboring As-As bonds (see Fig. 5a). The most favorable amorphization path IV for this  $\times 0$ - $\text{As}_4\text{S}_3$ -I molecule with  $\Delta E_f = 2.18$  kcal/mol is connected with matrix decomposition in two optimally-constrained sub-networks ( $n_c = 3.00$ ) depicted on Fig. 5c, these being composed of  $\text{AsS}_{3/2}$  pyramids ( $Z = 2.40$ ) and  $\text{As}_3\text{S}_{3/2}$  clusters ( $Z = 2.67$ ) keeping three neighboring homonuclear As-As bonds in triangle-like geometry. The latter are responsible for sharp 275  $\text{cm}^{-1}$  band ascribed to symmetric-stretch breathing mode



**Fig. 9** Competitive amorphization scenarios in nanostructured  $\text{As}_4\text{S}_4$ - $\text{As}_4\text{S}_3$  arsenicals driven from boundary compositions of As-rich molecular precursors  $\text{As}_4\text{S}_4$  and  $\text{As}_4\text{S}_3$ . The molecular precursors of most favorable network-forming clusters are also depicted. The optimally-constrained clusters with  $n_c = 3.00$  are inserted in green

boxes, while orange and blue colors are used respectively for over-constrained ( $n_c > 3.00$ ) and under-constrained clusters ( $n_c < 3.00$ ). In the cluster marking, terminated H atoms are grey colored, S and As atoms are yellow- and red-colored, and inter-cluster covalent bonds are denoted by respectively-colored sticks

of the basal  $\text{As}_3$ -rings in the Raman spectra of  $\text{As}_4\text{S}_3$ -type alloys [14, 17, 18, 20, 21, 28]. Thereby, in the current case, the amorphizing substance also demonstrates strong glass-forming ability due to optimally-constrained topology of covalent backbone ( $n_c = 3.00$ ), possessing double- $T_g$  relaxation with distinguishable glass-transition mid-points  $T_{g1}$  and  $T_{g2}$  as for  $\times 4$ -p- $\text{As}_4\text{S}_4$  clusters derived from pararealgar p- $\text{As}_4\text{S}_4$  molecule.

This amorphization path IV dominates in dimorphite  $\text{As}_4\text{S}_3$ -type arsenicals (see Fig. 9), the only competitive amorphization path V being related to incomplete destroying of  $\text{As}_4\text{S}_3$ -I molecule due to single  $\times 1$ -break stabilizing under-constrained matrix ( $n_c = 2.86$ ) with neighboring small rings in triangle and pentagon configurations (as shown in Fig. 5b). This variant is to be considered rather as defective in view of higher molecular-to-network barrier  $\Delta E_f = 2.46$  kcal/mol.

Thus, nanoamorphization in  $\text{As}_4\text{S}_4$ - $\text{As}_4\text{S}_3$  arsenicals dominates by clear tendency towards optimally-constrained structural network with  $n_c = 3.00$  stabilized via pathways I, III and IV (see Fig. 9), respective molecular-to-network transitions being accompanied by arsenical decomposition on stoichiometric ( $Z = 2.40$ ) and over-stoichiometric ( $Z > 2.40$ ) sub-networks via path III and IV. Competitive contribution of these amorphization scenarios is defined preferentially by arsenical composition, where higher barriers of molecular-to-network transition in dimorphite-type  $\text{As}_4\text{S}_3$  arsenicals ( $\Delta E_f > 2$  kcal/mol) allow  $\text{As}_4\text{S}_4$ - $\text{As}_4\text{S}_3$  alloys nominated as higher-crystalline ones, in full respect to terminology of Hruby [1].

The unified potential energy landscape showing diversity of molecular-to-network amorphization scenarios in the studied nanostructured arsenicals realized for boundary  $\text{As}_4\text{S}_4$  and  $\text{As}_4\text{S}_3$  components is shown on Fig. 10.

Under nanostructurization due to high-efficient external influence such as nanomilling, the role of  $\text{As}_4\text{S}_4$ -type arsenicals is mainly revealed through amorphization transitions from under-constrained realgar-type  $\times 0$ - $\beta$ - $\text{As}_4\text{S}_4$  molecule ( $n_c = 2.875$ ) supplemented by transitions from under-constrained pararealgar-type  $\times 0$ -p- $\text{As}_4\text{S}_4$  ones ( $n_c = 2.75$ ). The former dominates by appearance of network-forming optimally-constrained  $\times 1$ - $\beta$ - $\text{As}_4\text{S}_4$  clusters (having  $n_c = 3.00$  and molecular-to-network barrier approaching  $\Delta E_f = 0.71$  kcal/mol) along with over-constrained  $\times 3$ - $\beta$ - $\text{As}_4\text{S}_4$  clusters (having  $n_c = 3.25$  and  $\Delta E_f = 1.14$  kcal/mol). The latter dominates mainly by transformation towards  $\times 4$ -p- $\text{As}_4\text{S}_4$  clusters separating the arsenical matrix on two sub-networks composed of stoichiometric optimally-constrained  $\text{AsS}_{3/2}$  trigonal pyramids ( $Z = 2.40$ ,  $n_c = 3.00$ ) and As-rich non-stoichiometric over-constrained  $\text{As}_3\text{S}_{5/2}$  chains ( $Z = 2.55$ ,  $n_c = 3.36$ ). In this case, the degree of network decomposition in nanoarsenical (and, respectively, the parameters of double- $T_g$  relaxation) is

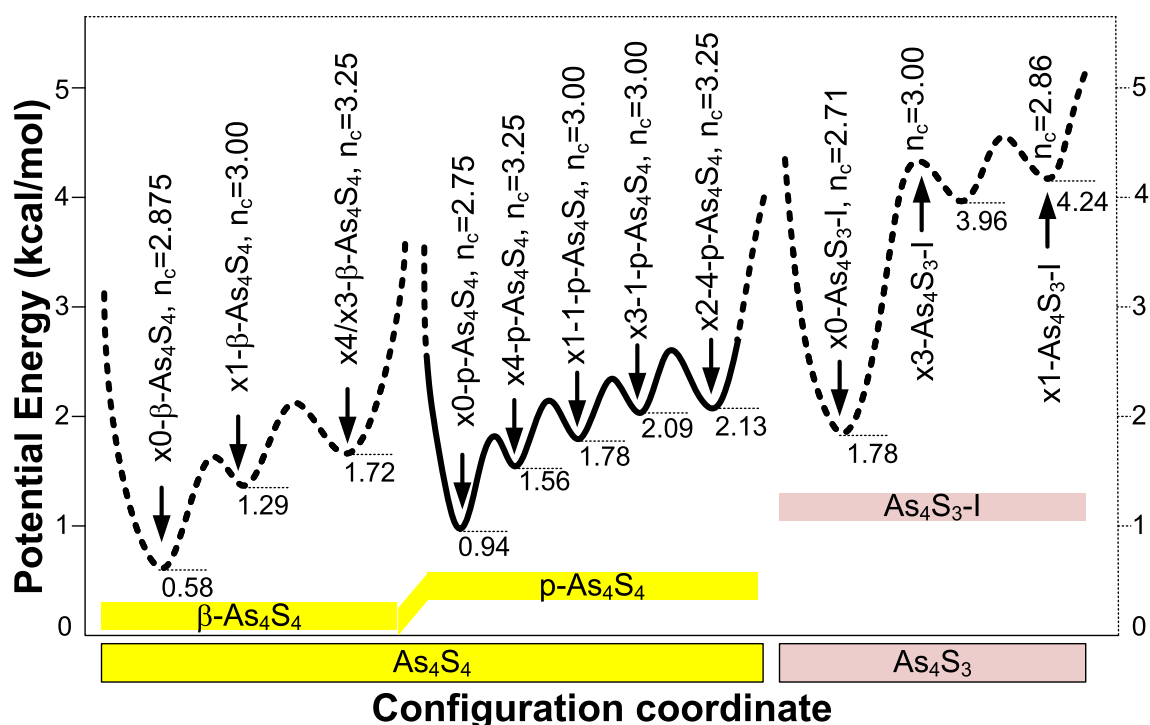
defined by completeness of preliminary alteration from  $\alpha/\beta$ - $\text{As}_4\text{S}_4$  phase to metastable pararealgar p- $\text{As}_4\text{S}_3$  phase through its intermediate precursor (such as  $\chi$ -phase  $\text{As}_4\text{S}_4$ ).

In  $\text{As}_4\text{S}_3$ -type arsenicals, main amorphization scenario is connected with transition from under-constrained dimorphite-type  $\times 0$ - $\text{As}_4\text{S}_3$ -I molecules ( $Z = 2.57$ ,  $n_c = 2.71$ ) possessing *triangle-like* configuration in the nearest arrangement of three neighboring homonuclear As-As bonds (as depicted in Fig. 5a) to their triple-broken  $\times 3$ - $\text{As}_4\text{S}_3$ -I derivatives. The respective structural transformations separate arsenical matrix on two optimally-constrained sub-networks (both having  $n_c = 3.00$ ) composed of  $\text{AsS}_{3/2}$  pyramids ( $Z = 2.40$ ) and over-stoichiometric As-rich  $\text{As}_3\text{S}_{3/2}$  clusters ( $Z = 2.67$ ) keeping the basal  $\text{As}_3$ -rings. This amorphization scenario can be only slightly disturbed (if any) by incomplete destroying of  $\text{As}_4\text{S}_3$ -I molecules owing to single  $\times 1$ -breaking in one of S atom positions, thus stabilizing intrinsically uniform but rather under-constrained (in view of  $n_c = 2.86$ ) network with cluster-forming energy approaching  $E_f = -4.24$  kcal/mol (see Fig. 9).

## Conclusions

Complete hierarchy of network-forming amorphization scenarios in  $\text{As}_x\text{S}_{100-x}$  nanoarsenicals within  $\text{As}_4\text{S}_4$ - $\text{As}_4\text{S}_3$  cut-Sect. ( $50 \leq x \leq 57$ ) is reconstructed employing materials-computational approach based on *ab-initio* quantum-chemical modeling code (CINCA).

Under nanostructurization caused by external influence such as high-energy mechanical milling, complicated inter-crystalline phase transformations towards nanoscopic high-temperature  $\beta$ - $\text{As}_4\text{S}_4$  polymorph accompanied by appearance of compositionally-invariant covalent-network amorphous phase are activated in these alloys. General amorphization trend under nanomilling obeys tending from molecular cage-like structures to optimally-constrained covalent networks which are isocompositional to the parent alloy. Optimal topological constitution of amorphous phase generated in nanoarsenicals is ensured by diversity of respective small-ring configurations incorporated in their covalent networks. Contribution of network-forming amorphization pathways in  $\text{As}_4\text{S}_4$ - $\text{As}_4\text{S}_3$  nanoarsenicals is defined by their chemistry with higher molecular-to-network transition barriers proper for  $\text{As}_4\text{S}_3$ -rich alloys (more than  $\sim 2$  kcal/mol). The generated amorphous phase is intrinsically decomposed, possessing double glass-transition temperature  $T_g$  relaxation due to stoichiometric ( $x = 40$ ) and non-stoichiometric ( $x > 40$ ) sub-networks, which are respectively built of  $\text{AsS}_{3/2}$  pyramids and As-rich entities keeping two separated As-As bonds derived from realgar-type molecules, two neighboring As-As bonds



**Fig. 10** Unified potential energy landscape showing diversity of main molecular-to-network amorphization transitions in nanostructured  $\text{As}_4\text{S}_4$ - $\text{As}_4\text{S}_3$  arsenicals, restricted for boundary  $\text{As}_4\text{S}_4$  (left) and  $\text{As}_4\text{S}_3$  (right) compositions. The calculated cluster-forming energies

( $E_p$ ) are right-side denoted near energy wells corresponding to molecular clusters and their most favorable network derivatives pointed out by arrows (the atom-averaged topological constraints  $n_c$  are indicated)

derived from pararealgar-type molecules and/or three neighboring As-As bonds in triangle-like geometry derived from dimorphite-type molecules. Compositional invariance of nanomilling-derived amorphous phase in  $\text{As}_x\text{S}_{100-x}$  arsenicals within  $\text{As}_4\text{S}_4$ - $\text{As}_4\text{S}_3$  cut-section is ensured by network-forming clusters generated in a growing sequence with average coordination number  $Z$ : ( $\text{As}_2\text{S}_{4/2}$ ,  $Z = 2.50$ ) – ( $\text{As}_3\text{S}_{5/2}$ ,  $Z = 2.55$ ) – ( $\text{As}_3\text{S}_{3/2}$ ,  $Z = 2.67$ ). Full diversity of molecular-to-network amorphization pathways in the studied  $\text{As}_4\text{S}_4$ - $\text{As}_4\text{S}_3$  nanoarsenicals is specified on unified potential energy landscape for boundary  $\text{As}_4\text{S}_4$  and  $\text{As}_4\text{S}_3$  components.

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**Data Availability** The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

## Declarations

**Conflict of interest** The authors declare that they have no conflict of interest.

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